USE OF 8-HYDROXYQUINOLINE IN SEPARATIONS OF ALUMINUM

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ABSTRACT

Many analytical operations leave aluminum associated with elements, such as phosphorus, vanadium, arsenic, molybdenum, uranium, fluorine, boron, columbium, tantalum, and beryllium. The data presented show that aluminum can be quantitatively precipitated and separated from these elements by the use of the reagent 8-hydroxyquinoline, provided proper conditions are established.

CONTENTS

I. GENERAL CONSIDERATIONS

In analyses of material containing aluminum, preliminary separations, such as filtration after precipitation with an excess of sodium hydroxide or extraction of alkali carbonate or hydroxide melts with water, often leave aluminum still associated with elements, such as phosphorous, vanadium, arsenic, molybdenum, uranium, fluorine, boron, columbium, tantalum, and beryllium. A method that will yield a precipitate containing aluminum alone when applied to such mixtures is much needed. The experimental work that is to be described goes to show that precipitation with 8-hydroxyquinoline can be made to fulfill this requirement, provided proper conditions are established.

The use of 8-hydroxyquinoline (C_9H_6NOH, and variously called o-oxychinoline, 8-oxychinolin, oxin) for the determination of certain elements has been described by Berg,[1] Hahn and Vieweg,[2] and Robitshek.[3] These researches deal primarily with the determination of

[1] R. Berg, Z. anal. Chem., **70**, p. 341; 1927; **71**, pp. 23, 171, 321, 369; 1927; **72**, p. 177; 1928; **76**, p. 191; 1929.
[2] F. L. Hahn and K. Vieweg, Z. anal. Chem., **71**, p. 122; 1927.
[3] J. Robitshek, J. Am. Cer. Soc., **11**, p. 587; 1928.

elements such as copper, aluminum, cadmium, bismuth, zinc, and magnesium in pure solutions. As regards aluminum, it has been shown that it can be completely precipitated by 8-hydroxyquinoline in either ammoniacal or feebly acid solutions. The precipitate that is obtained has the composition expressed by the formula $Al(C_9H_6ON)_3$ and can be weighed as such after drying at 110° C.[4] It is also stated that the precipitate can be converted to aluminum oxide by igniting it under a cover of anhydrous oxalic acid [5] or dissolved in acid and titrated with a standard solution of potassium bromate-potassium bromide.[5] In such a titration 12 atoms of bromine represent 1 atom of aluminum.

Of the various methods that have been recommended for the treatment of the precipitate the authors have tried only direct ignition to the oxide. In such tests as were made difficulty apparently due to volatilization of the salt was experienced. As a result, in the experiments to be described, the actual determination of aluminum was made by decomposing the filter and precipitate with nitric and sulphuric acids, precipitating the aluminum as hydroxide, igniting to the oxide, and correcting for silica. This procedure was all the more attractive in that the effect of contaminating compounds was not minimized, as might be the case if calculations were based on the small factor (0.1110 for Al_2O_3) used for the dried salt, or hidden, as might be the case if titration were employed.

Tests of the ignited alumina generally showed complete removal of the other constituent or its presence in such minute quantities as to be wholly without effect on the determination.

II. SEPARATIONS

1. SEPARATION OF ALUMINUM FROM PHOSPHORUS

The separation of aluminum from phosphorus is satisfactorily accomplished by precipitating with 8-hydroxyquinoline in ammoniacal solution, as follows: To the solution slightly acid with sulphuric or hydrochloric acid and containing not more than 0.1 g of aluminum oxide in 100 ml of solution, add an excess of a 2.5 per cent solution of 8-hydroxyquinoline in diluted acetic acid,[6] then dilute ammonium hydroxide until alkaline, and finally an excess of 5 ml of strong ammonium hydroxide in 100 ml of solution. Warm to 60° to 70° C. and digest at this temperature until the precipitate becomes dense and crystalline. Cool, preferably in ice water, filter through a tight paper

[4] R. Berg, loc. cit.; I. M. Kolthoff and E. B. Sandell (J. Am. Chem. Soc., 50, p. 1900; 1928) obtained satisfactory results by drying at 120° to 140° C

[5] See footnote 1, p. 91.

[6] Prepared by triturating 2.5 g of 8-hydroxyquinoline and 5 ml of glacial acetic acid and pouring the resulting solution into 100 ml of water at 60° C. After cooling the solution is filtered. 1 ml of this solution suffices to precipitate 2.9 mg of alumina in pure solution. An excess of the reagent does no harm; in any case enough should be used to color the solution yellow.

and wash the precipitate thoroughly with a cold dilute solution of ammonium hydroxide (1:40) containing 25 ml of the reagent, previously neutralized with ammonium hydroxide, in 1 liter. Treat the precipitate and paper with nitric and sulphuric acids to destroy organic matter and precipitate the aluminum with ammonium hydroxide as usual. The results that can be obtained with the method are indicated by the data shown in Table 1.

TABLE 1.—*Separation of aluminum from phosphorus*

[Final volume of solution 200 ml]

Al_2O_3 taken	P_2O_5 taken	Al_2O_3 found	Difference	Remarks
g	*g*	*g*	*g*	
0.0945	0.05	0.0942	−0.0003	Single precipitation.[1]
.0945	.05	.0940	−.0005	Do.
.0945	.05	.0946	+.0001	Do.
.0945	.05	.0945	.0000	Double precipitation.
.0945	.05	.0944	−.0001	Do.
.0047	1.000	.0048	+.0001	Single precipitation in presence of H_2O_2.
.0047	1.000	.0048	+.0001	Do.

[1] After single precipitations in a solution containing 0.05 g of Al and in another containing 0.05 g of Al and 1 g of P_2O_5, no aluminum could be found in the filtrates and the precipitate obtained in the second solution contained less than 0.2 mg of P_2O_5.

2. SEPARATION OF ALUMINUM FROM VANADIUM

Complete separation of aluminum from vanadium can not be obtained by the preceding method, even by repeated precipitation, regardless of whether the vanadium is quadrivalent or quinquevalent. However, complete separation is easily obtained if vanadium is oxidized to a still higher valency; as, for example, by precipitating in a solution containing hydrogen peroxide. The only modification that is needed in the method as described in 1 is the addition of 10 to 15 ml of a 3 per cent solution of hydrogen peroxide before the 8-hydroxyquinoline is added. The results which can be obtained with the method are shown in Table 2.

TABLE 2.—*Separation of aluminum from vanadium*

[Final volume of solution 200 ml]

Al_2O_3 taken	V_2O_5 taken	Al_2O_3 found	Difference	Remarks
g	*g*	*g*	*g*	
0.0945	0.05	0.0947	+0.0002	Single precipitation.[1]
.0945	.05	.0945	.0000	Do.
.0945	.05	.0944	−.0001	Double precipitation.
.0945	.05	.0944	−.0001	Do.

[1] After single precipitation in a solution containing 0.05 g of Al and in another containing 0.05 g of Al and 0.5 g of V_2O_5, no aluminum could be found in the filtrates and the precipitate obtained in the second solution contained less than 0.2 mg of V_2O_5.

3. SEPARATION OF ALUMINUM FROM TANTALUM, COLUMBIUM, TITANIUM, MOLYBDENUM, ARSENIC, FLUORINE, AND BORON

The separation of aluminum from arsenic, fluorine, or boron can be satisfactorily carried out in ammoniacal solution as described under 1. For separations from tantalum, columbium, titanium, and molybdenum, hydrogen peroxide to form peroxidized compounds must be added as described in section 2.

Results are shown in Table 3.

TABLE 3.—*Separation of aluminum from boron, fluorine, arsenic, columbium, tantalum, titanium, and molybdenum*

[Final volume of solution 200 ml]

Contaminant	Al_2O_3 taken	Al_2O_3 found	Difference	Confirmatory experiments
	g	*g*	*g*	
[1] 1 H_3BO_3	0.0945	0.0941	−0.0004	No aluminum was found in the filtrate and no boron in the precipitate after a single precipitation of 0.05 g of aluminum in the presence of 0.5 g of B_2O_3.
[1] 0.20NaF	.0945	.0942	−.0003	No aluminum was found in the filtrate and no fluorine in the precipitate after a single precipitation of 0.05 g of Al in the presence of 5.0 g of NaF.
[1] 0.05As_2O_5	.0945	.0940	−.0005	No aluminum was found in the filtrate and less than 0.5 mg of arsenic was found in the precipitate after a single precipitation of 0.05 g of aluminum in the presence of 0.2 g of As_2O_5. No aluminum was found in the filtrates and no arsenic in the precipitate after a double precipitation of 0.05 g Al in the presenc of 1 g of As_2O_5.
[2] 0.05Cb_2O_5	.0945	.0941	−.0004	The precipitate contained no Cb_2O_5 after double and less than 1 mg of Cb_2O_5 after single precipitation in a solution containing 0.05 g of Al and 0.2 g of Cb_2O_5.
[2] 0.05Ta_2O_5	.0945	.0945	.0000	The precipitate contained no Ta_2O_5 after double and less than 1.5 mg of Ta_2O_5 after single precipitation in a solution containing 0.05 g of Al and 0.2 g of Ta_2O_5.
[2] 0.05TiO_2	.0945	.0943	−.0002	The precipitate contained less than 0.1 mg of TiO_2 after double and less than 1 mg of TiO_2 after single precipitation in a solution containing 0.05 g of Al and 0.2 g of TiO_2.
[2] 0.05MoO_3	.0945	.0938	−.0007	No aluminum was found in the filtrates and less than 0.3 mg of MoO_3 in the precipitate after a double precipitation of 0.05 g of Al in the presence of 0.05 g of MoO_3.

[1] Single precipitation. [2] Double precipitation.

4. SEPARATION OF ALUMINUM FROM BERYLLIUM

It has already been shown by Kolthoff and Sandell [7] that a satisfactory separation of aluminum from beryllium can be had by precipitating with 8-hydroxyquinoline in dilute acetic acid solution, as follows: Warm a slightly acid solution of aluminum and beryllium to 50° to 60° C. and treat with an excess of an acetic acid solution of the precipitant. Add 2 *N* ammonium acetate until a permanent precipitate is obtained and then 20 to 25 ml in excess. Let settle, filter through a Jena glass or a porous porcelain crucible, wash with cold water, and dry at 120° to 140° C. The beryllium in the filtrate may be determined by precipitating with ammonia and igniting to the oxide.

[7] See footnote 4, p. 92.

5. SEPARATION OF ALUMINUM FROM URANIUM

Successful separations of aluminum from uranium can not be obtained by the methods given for phosphorus or vanadium. However, satisfactory results follow if ammonium carbonate is substituted for ammonia in the method outlined for the separation of aluminum from phosphorus. In such case prepare a faintly acid solution containing the aluminum, uranium, and 8-hydroxyquinoline, cautiously neutralize with a saturated solution of ammonium carbonate, add an excess of 25 ml per 100 ml of solution, and heat to about 50° C., taking care to avoid excessive effervescence caused by too rapid heating. The performance of the method is shown in Table 4.

TABLE 4.—*Separation of aluminum from uranium*

[Final volume of solution 200 ml]

Al_2O_3 taken	UO_3 taken	Al_2O_3 found	Difference	Remarks
g	*g*	*g*	*g*	
0.0945	0.05	0.0946	+0.0001	Double precipitation.[1]

[1] After single precipitations in a solution containing 0.05 g of Al and in another containing 0.05 g of Al and 0.2 g of UO_3, no aluminum could be found in the filtrates, and the precipitate obtained in the second solution contained no uranium.

III. APPLICATIONS

In tests on the Bureau of Standards standard sample of ferrovanadium No. 60 and ingot iron No. 55, in which speed rather than accuracy was sought, the results in Table 5 were obtained.

TABLE 5.—*Determination of aluminum in ferrous materials*

Material	Weight of sample	Al present	Al found
	g	*Per cent*	*Per cent*
Ferrovanadium No. 60 [1]	1.000	12.5	12.10
Ingot iron [1]	2.000	[2] 1.0	.96
Do. [3]	2.000	[2] 1.0	.95
Do. [3]	2.000	[2] .05	.03
Do. [3]	2.000	[2] .05	.04

[1] Single precipitation. [2] Added as pure aluminum. [3] Double precipitation.

In these analyses the acid solution of the material was partially neutralized with sodium hydroxide and poured slowly and with stirring into enough of a 5 per cent solution of the latter to make the final volume exactly 500 ml. A 250 ml aliquot portion was then filtered, acidified with sulphuric acid, and the aluminum precipitated with 8-hydroxyquinoline as in (1) in the case of ingot iron and as in in (2) with the ferrovanadium. Low results in such tests are to be expected, as there is always some retention of aluminum by the sodium hydroxide precipitate.

Another interesting application of 8-hydroxyquinoline is for the detection of impurities, such as iron and aluminum, in phosphoric acid or alkali phosphates. In such tests the reagent will give precipitates in solutions that remain absolutely clear when treated with ammonia alone. For example, ammonium hydroxide gave no precipitate whatever in a 25 ml portion of phosphoric acid (specific gravity 1.71) which had been diluted to 500 ml and treated with aluminum chloride equivalent to 0.001 g of Al_2O_3; while a similarly prepared portion gave a precipitate with 8-hydroxyquinoline which weighed 0.0025 g when ignited. A third 25 ml portion of the acid to which no aluminum was added gave a precipitate weighing 0.0015 g, exactly 0.001 g less than was obtained from the portion that was adulterated with 0.001 g of Al_2O_3, and representing 0.0035 per cent of "matter precipitable by 8-hydroxyquinoline" in the phosphoric acid. The precipitate produced by the reagent in an ammoniacal solution contains, in addition to the aluminum, all of the iron and no doubt other elements, such as magnesium, that may be present in the phosphoric acid and are normally precipitated in ammoniacal solution by 8-hydroxyquinoline.

IV. SUMMARY

The data presented show that precipitations with 8-hydroxyquinoline serve to separate aluminum from phosphorus, arsenic, fluorine, and boron if made in ammoniacal solutions, from tantalum, columbium, titanium, and molybdenum if made in ammoniacal solutions containing hydrogen peroxide, and from uranium if made in ammonium carbonate solutions. Others have shown that aluminum can also be separated from beryllium if precipitation is made in acetic acid solution.

These separations are of especial interest in that many of the preliminary separations that are usually made for aluminum leave it still associated with the most of these elements.

WASHINGTON, April 6, 1929.